

PVTx Measurements for H₂O + Methanol Mixtures in the Supercritical Region

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The volumetric (PVTx) properties of H₂O-methanol mixtures were measured in a range of temperatures from 423 to 653 K and pressures between 5 and 40 MPa at concentrations from 0 to 1 mole fraction. Measurements were made with a constant-volume piezometer surrounded by a precision thermostat. The apparatus consisted of an air thermostat, a piezometer, lines for filling and extracting samples, devices for temperature measurement and control, and instruments for pressure measurements. The temperature inside the thermostat was maintained uniform within 5 mK. The volume of the piezometer ($32.68 \pm 0.01 \text{ cm}^3$) was previously calibrated from the established PVT values of pure water (IAPWS-95). Uncertainties of the density, temperature, and pressure measurements are estimated to be 0.15 %, 10 mK, and 0.05 %, respectively. The uncertainty in composition measurement is 0.001 mole fraction. The measured densities were used to calculate excess molar volumes, those values were compared with values calculated with a reliable model by Simonson *et al.* The measurements were also compared with values calculated with an equation-of-state model. The measured densities were also used to calculate values of the Krichevskii parameter; the derived value of the Krichevskii parameter was compared with a value estimated from the critical loci and vapor-pressure data. The method of isochoric break points was used to extract the phase transition temperatures and pressures for each measured isochore. The densities of H₂O-methanol mixtures at saturation were also extracted from two-phase PVTx measurements using an extrapolating technique.